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TESTS OF THEORIES FOR NONPLANAR GROWTH DURING RAPID ALLOY SOLIDIFICATION

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Abstract

During rapid solidification, kinetically suppressed solute partitioning at the crystal/melt interface, as well as kinetic interfacial undercooling, become important. Both of these effects have significant stabilizing influences on a planar interface during rapid solidification. We review experimental tests we have performed of models for the transition from planar to cellular growth, and for the velocity-undercooling function of the dendrite tip, in the velocity regime where nonequilibrium interface kinetics are important.

Introduction

The phase selection, growth velocity, chemical composition, long-range order, and microstructure of a solidifying phase or phases are functions of the local conditions at the solid/liquid interface, e.g., temperature, composition, orientation, curvature, and crystal structure. Our research has been aimed at illuminating how the kinetics of atom movements leads to these functions and has permitted us to take several steps toward predictive capability for the production of materials under rapid solidification processing conditions.

The modeling of an alloy solidification process typically treats the transport of solute and heat through the bulk of one or both of the phases involved in the transformation. In rapid solidification, deviations from local interfacial equilibrium become evident [1], and interface kinetic boundary conditions must replace local equilibrium boundary conditions for a quantitative or, sometimes, even qualitative description of solidification behavior [2]. Substantial deviations from local equilibrium occur as the interface velocity approaches the diffusive speed v_D -- the ratio of the diffusion coefficient across the interface to the interatomic spacing [3]. These deviations have significant implications for interface morphology and microstructure formation in rapid solidification, leading to dramatically enhanced stability against cellular breakdown of a planar interface, and drastically altered dendrite growth conditions.

Two practical applications of the phenomena of enhanced interface stability in rapid solidification are worthy of note. Jet engine turbine disks are mass produced by rapid solidification and powder processing. In this case, rapid solidification produces a supersaturated solid that is the starting point for subsequent thermomechanical processing to produce a product with the desired mechanical properties. Also, there is currently some very active research in "pulsed laser annealing" or "laser thermal processing" of silicon [4]. In this case, rapid solidification is used either to make very shallow p/n junctions to accommodate shrinking transistor size, or to make polycrystalline thin film transistors for flat-panel displays.

This processing method has advantages for dopant incorporation at high concentrations into electrically active substitutional lattice sites.

Experiments and Results

We used rapid solidification following pulsed laser melting to permit simple but accurate measurements and calculations of important interface variables such as the interface temperature T , the interface velocity v , and the solute mole fraction X_S on the solid side and X_L on the liquid side of the moving interface -- variables that cannot be measured in less constrained solidification situations.

Our experiments showed that the Continuous Growth Model without solute drag [5] accounts well for the deviations from local equilibrium with the interface response being described by

$$k(v) = \frac{k_e + (v/v_D)}{1 + (v/v_D)} ; \quad (1)$$

and

$$v(T, X_S, X_L) = v_C(T) \left[1 - \exp \left(\frac{X_S \Delta \mu_B + (1 - X_S) \Delta \mu_A}{k_B T} \right) \right] , \quad (2)$$

where the partition coefficient k is X_S/X_L ; $\Delta \mu_B$ and $\Delta \mu_A$ are the chemical potentials of solute and solvent, respectively, in the solid at the interface minus their values in the melt at the interface; and v_D and v_C are the two kinetic mobilities in the model. The crystallization speed v_C is the maximum crystallization speed at infinite driving force [6], which can approach the speed of sound [7]. Equations (1) and (2) are applicable to dilute alloys and (2) can be further simplified [6,8], but for non-dilute alloys, corrections [5] to Eq. (1) must be used.

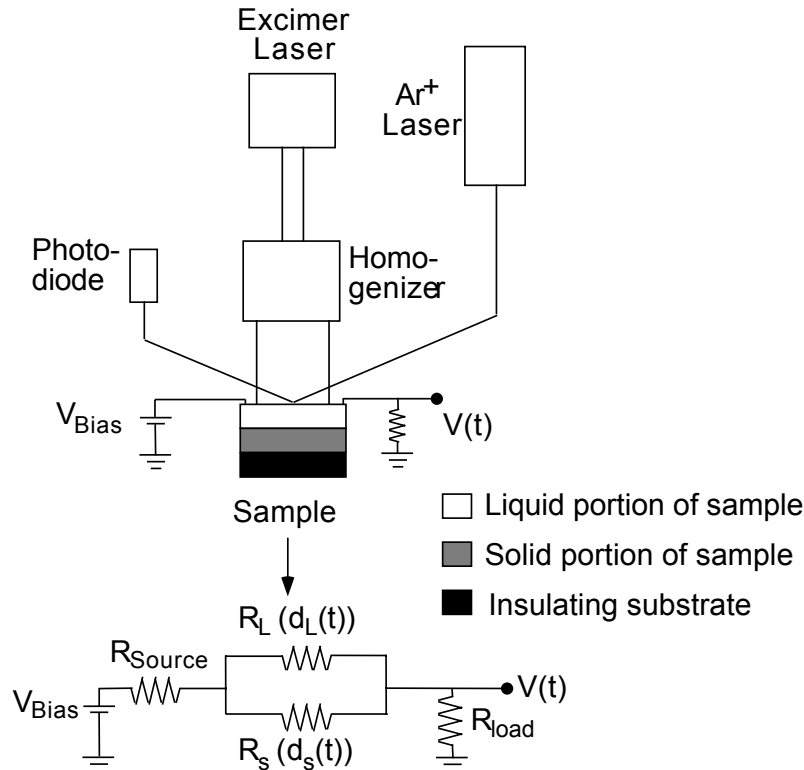


Figure 1. Transient conductance measurement of interface velocity during pulsed laser melting and equivalent circuit. Unless and until the interface becomes non-planar, the sample may be treated as two resistors in parallel.

A typical experimental geometry for measuring the interface velocity is shown in Fig. 1. Thin film patterning techniques are used to create a sample with an electrical path of length ~ 1 mm and width ~ 0.1 mm in a film ~ 100 nm thick, permitting the resistivity change upon melting to dominate the transient conductance signal. A spatially uniform pulsed excimer laser enforces plane-front melting and solidification. A low-power Ar^+ probe laser determines when the surface melts and solidifies, which is sometimes necessary for corroboration of the transient conductance data. Solute depth profiles are measured with ~ 1 nm resolution before and after each solidification experiment. Because the molten layer is too thin for convection, combining these measurements with a numerical solution of the 1-D diffusion equation permits the determination of k and v and the establishment of Eq. (1) experimentally. An extension of this technique to permit the measurement of temperature transients, by inserting an electrically isolated metallic "resistance temperature detector" between the sample film and the substrate, permitted us to establish Eq. (2) experimentally in collaboration with M.O. Thompson [9].

The use of the boundary conditions (1) and (2) instead of local interfacial equilibrium makes a big difference in the predictions for dendritic growth. In collaboration with D.M. Herlach, we performed a parameter-free test of dendrite growth theory [10]. For the same dilute Ni(Zr) alloy, we measured v_D with pulsed laser melting, and the dendrite tip $v(T)$ function was measured in D.M. Herlach's laboratory. We showed that the LKT-BCT (Lipton-Kurz-Trivedi [11]-Boettinger-Coriell-Trivedi [12]) theory agrees with our data with no adjustable parameters, using a value of the stability parameter $\sigma^* = 1/(4\pi^2)$ taken from the marginal stability criterion. The measured and predicted $v(T)$ function is shown in Fig. 2(a), the dendrite tip operating conditions are shown in Fig. 2(b-c), and the calculated contributions to the total bath undercooling are shown in Figs. 2(d). Subtleties associated with the relationship between marginal stability and "solvability theory" for undercooled cubic alloys are discussed in reference [10].

The use of the boundary conditions (1) and (2) instead of local interfacial equilibrium dramatically stabilizes an interface against cellular breakdown. We performed a parameter-free test of the theory predicting the critical solute concentration that destabilizes a planar crystal/melt interface in the high-velocity regime where nonequilibrium interface kinetics are important [13]. After pulsed laser melting of Si(Sn), samples remained microsegregation-free with near perfect crystallinity at Sn compositions up to 10 times the maximum equilibrium solubility and 100 times that predicted by linear stability theory with local interfacial equilibrium, as shown in Fig. 3. Our measurements agree with the predictions of linear stability theory [14,15] when it incorporates a velocity-dependent partition coefficient and a thermodynamically consistent kinetic liquidus [6,8], and contains no adjustable parameters. We also found a systematic increase of the breakdown concentration with increasing deviation from steady-state conditions, which is not addressed by stability theories and seems to correlate with the concentration gradient just prior to breakdown.

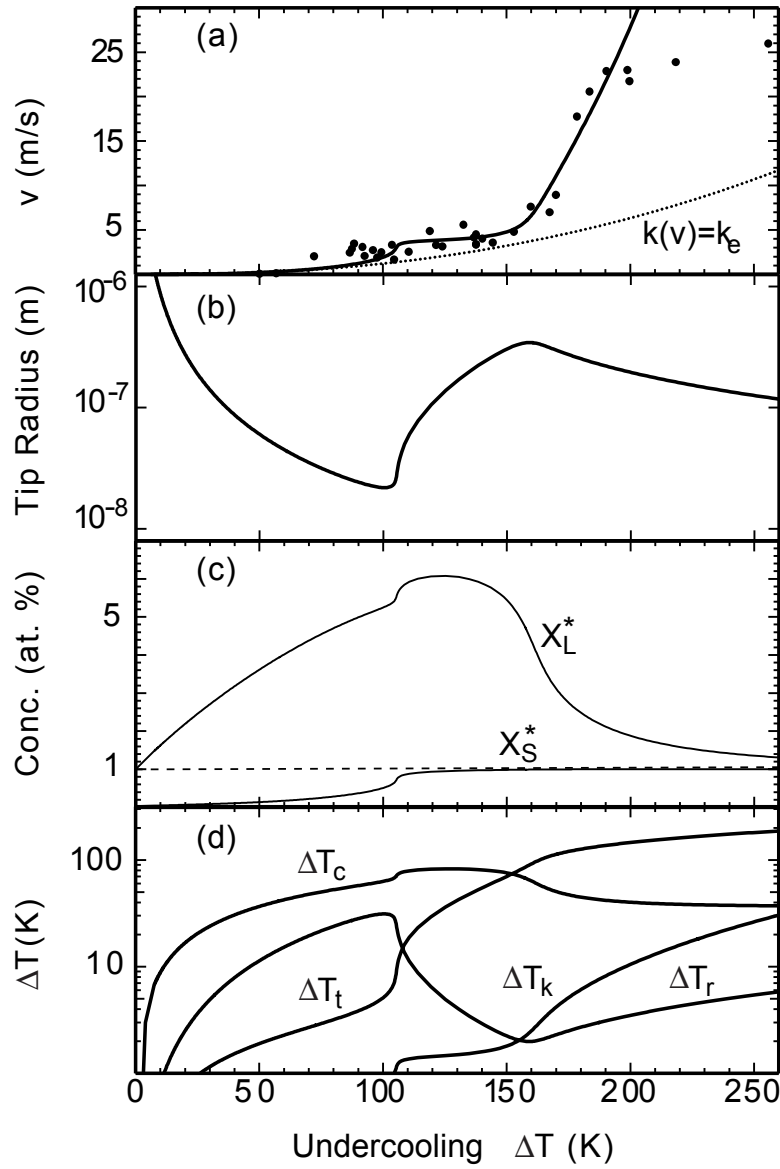


Figure 2. Dependence on total bath undercooling of various quantities [10]. (a) Dendrite growth velocity, as measured on a $\text{Ni}_{99}\text{Zr}_{01}$ alloy (dots). Solid line gives the prediction of the LKT-BCT theory with no adjustable parameters, using values of interface diffusive speed and melt-phase diffusivity measured directly in pulsed laser melting experiments on the same alloy. Dotted line gives the corresponding predictions if local interfacial equilibrium is assumed. (b) Dendrite tip radius predicted from marginal stability. (c) Solute concentrations in the melt and in the solid at the dendrite tip computed using LKT-BCT theory. (d) Semilog plot of the individual undercooling contributions: thermal undercooling ΔT_t , constitutional undercooling ΔT_c , curvature undercooling ΔT_r , and kinetic interface undercooling ΔT_k .

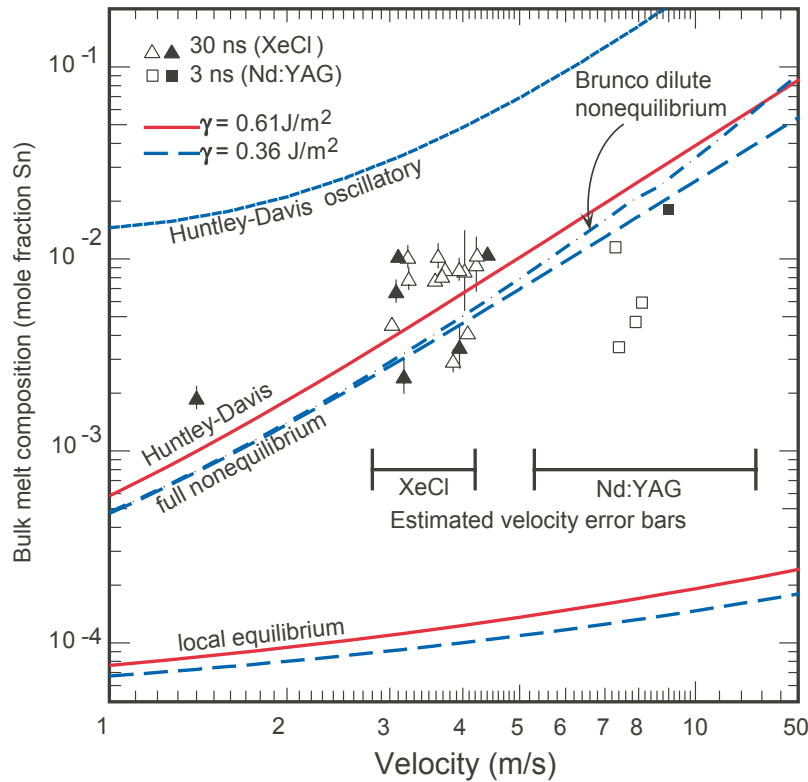


Figure 3. Parameter-free test of cellular breakdown theory, from [13]. Critical concentration for cellular breakdown vs. solidification velocity for Si(Sn) with Sn compositions ranging from 0.2 to 1 at.%. High velocities attained with 3 ns Nd:YAG laser; low velocities attained with 30 ns XeCl laser. Two differing literature values of the interfacial tension are used as input to theory. Local equilibrium predicts breakdown at a concentration two orders of magnitude too small. In contrast, including nonequilibrium interface kinetics accounts for experimental results very well. Experiments cannot distinguish between Huntley-Davis "full nonequilibrium" steady branch [14] and Brunco dilute nonequilibrium [15] models.

Conclusions

During rapid solidification, kinetically suppressed solute partitioning at the crystal/melt interface, as well as kinetic interfacial undercooling, have significant influences on interface stability during rapid solidification. The Continuous Growth Model without solute drag provides a model for the resulting interface boundary conditions that has been tested experimentally and that can be readily incorporated into theories for microstructure formation. The predictions of the LKT-BCT theory, which includes these boundary conditions, agrees well with our data on the dendrite tip operating conditions with no adjustable parameters. The predictions of linear stability theory for a planar interface, incorporating these boundary conditions, accounts well for our data on the critical solute concentration that destabilizes a planar crystal/melt interface, with no free parameters.

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